Supporting Information for

SBE-Type Metal-Substituted Aluminophosphates: Detemplation and Coordination Chemistry

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Experimental Section

UV-vis Absorption Spectroscopy

UV-*vis* absorption spectra were collected at room temperature using a Varian Cary 500 Scan UV-*vis* spectrometer in single-beam mode. Samples were dehydrated prior to measurements to remove all adsorbed water and prepared in the form of KBr pellets. To confirm the absence of absorption bands in the region measured, a background spectrum of KBr pellets was recorded.

X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) spectra were recorded using a Perkin Elmer PHI 5600ci ESCA system, employing an Al-Kα polychromatic source (1486.6 eV, 350 W, 15 kV). The takeoff angle was 45º. Wide scan survey and multiplex spectra were obtained with pass energies of 187.85 eV and 58.70 eV, respectively for the electron energy analyzer. The working pressure was lower than 10^{-9} Pa. All the binding energies reported were corrected utilizing the XPS signal of the carbon contamination peak (C_{1s}) at 284.5 eV of an internal standard. Extended spectra (survey) were collected in the range 0 -1200 eV (1 eV step, 1.6 s $step^{-1}$). Detailed spectra were recorded for the following regions: Al_{2p}, N_{1s}, C_{1s}, Co_{2p}, P_{2p} and O_{1s}, (1 eV step, 0.25 s $step^{-1}$).

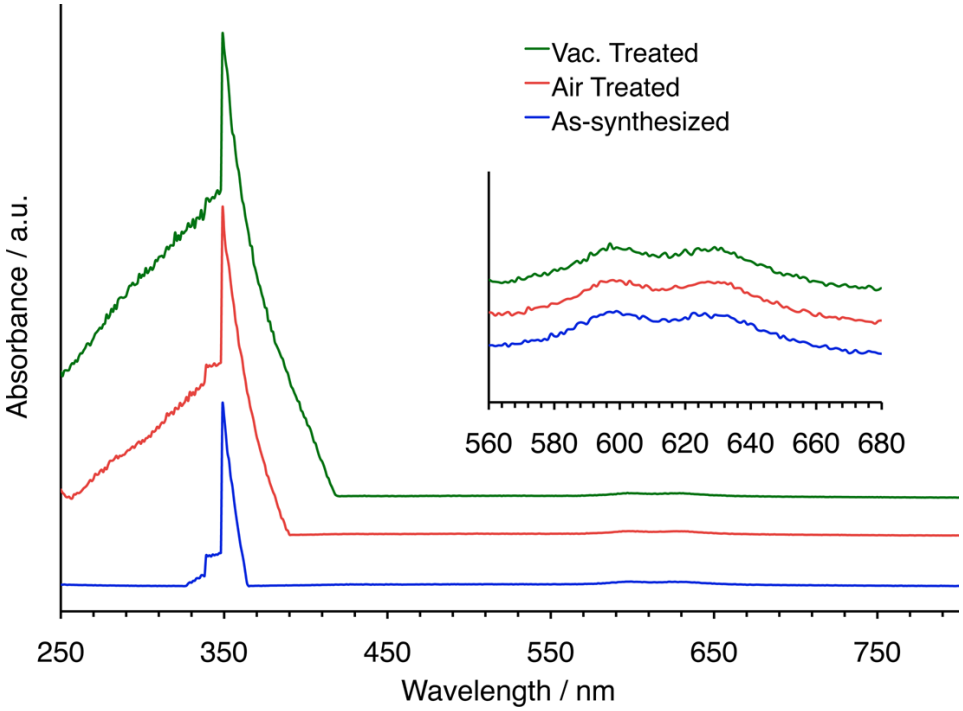


Figure S1. UV-*vis* absorption spectra of as-synthesized and treated Mn-SBE samples.

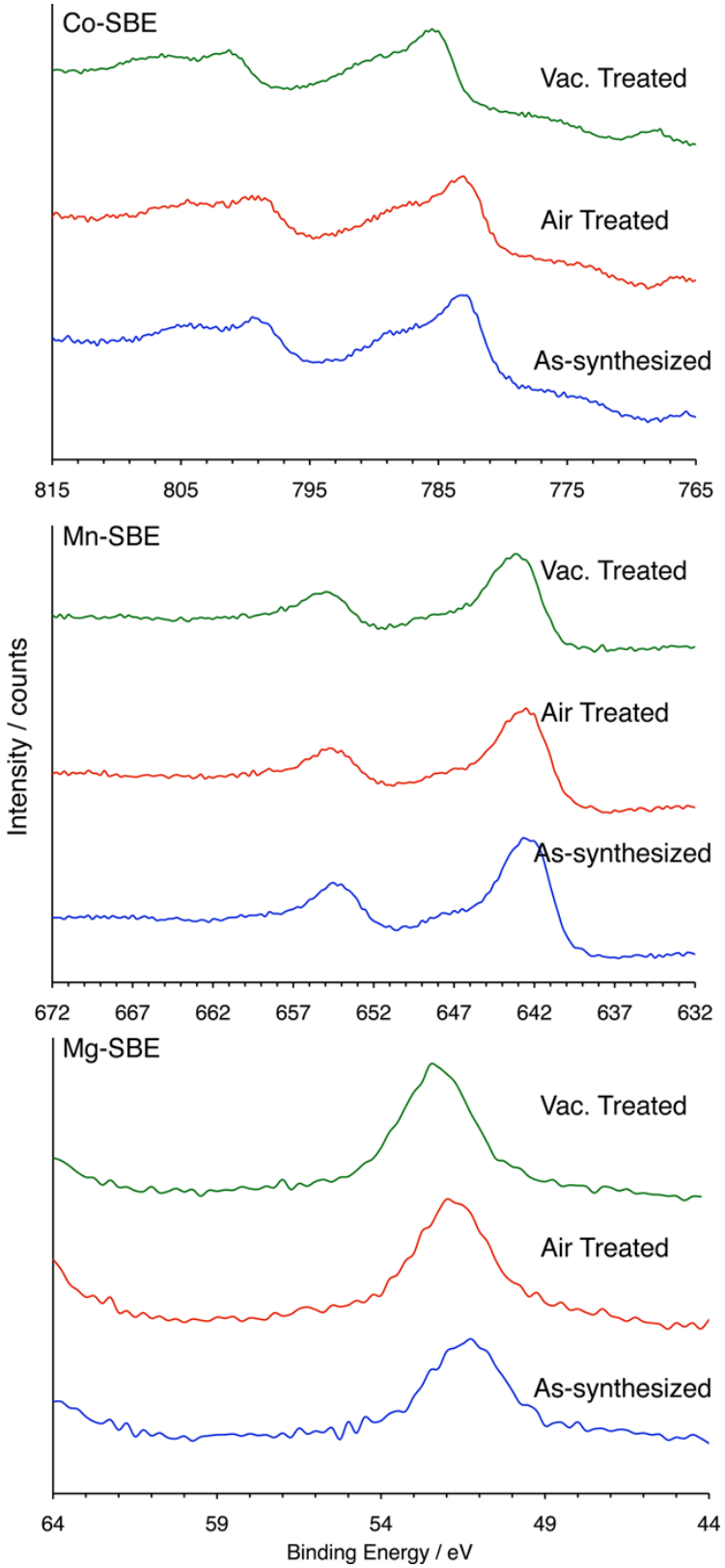


Figure S2. XPS spectra for as-synthesized and treated SBE samples.

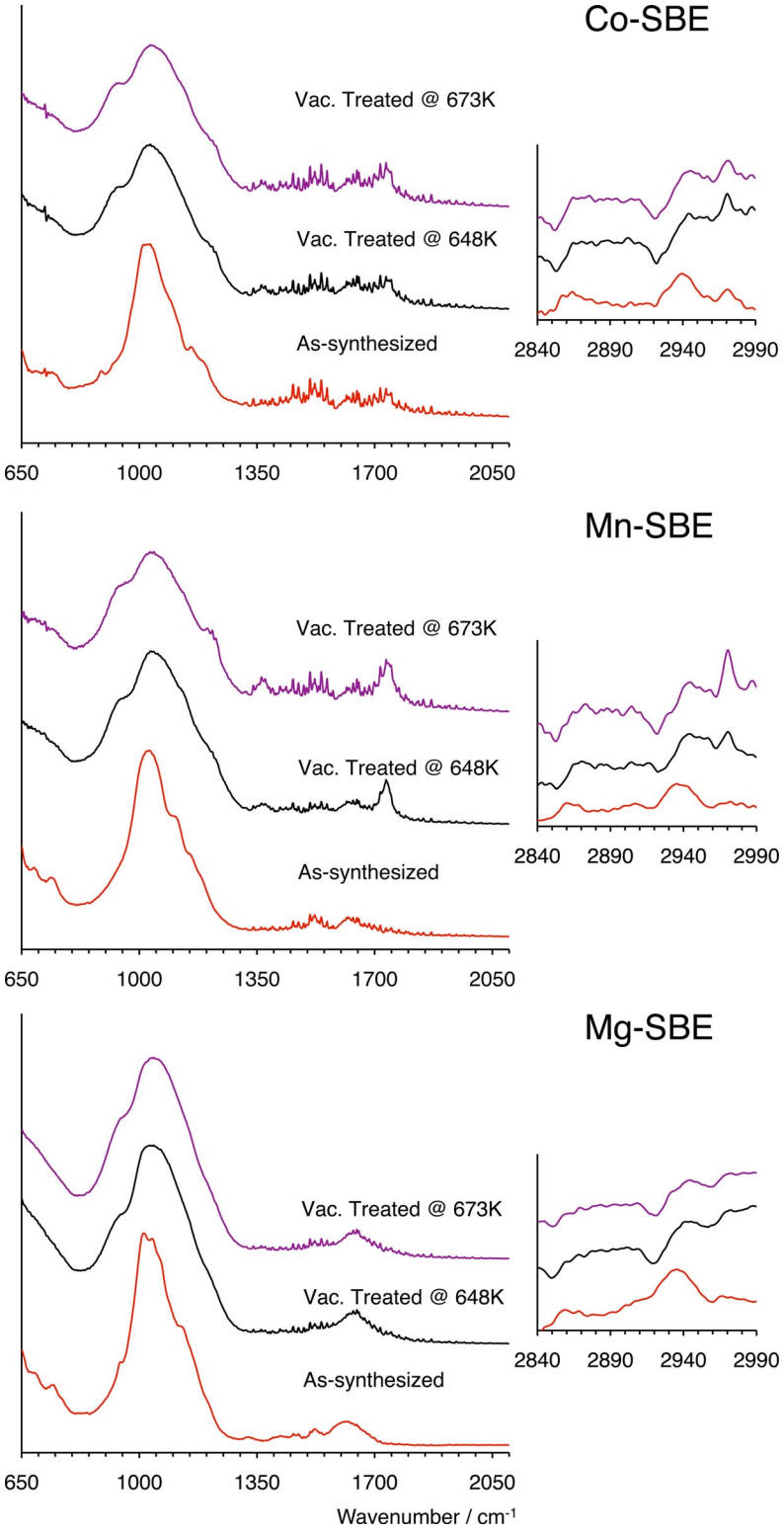
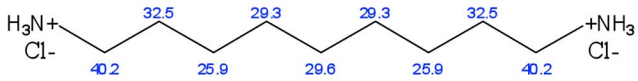
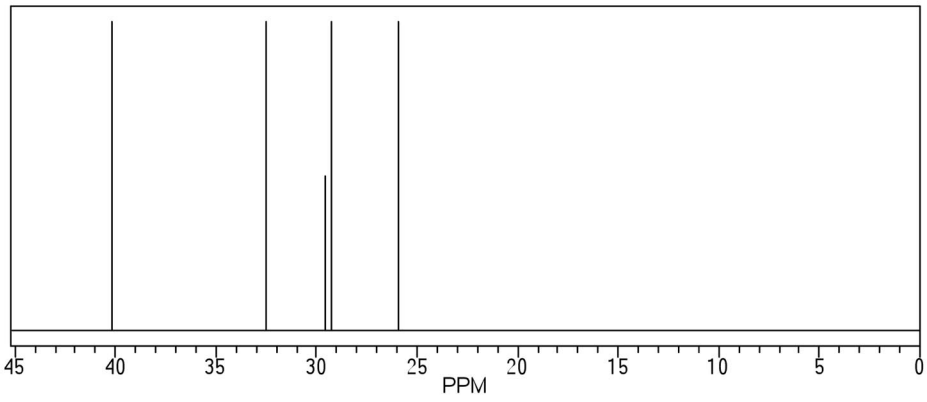


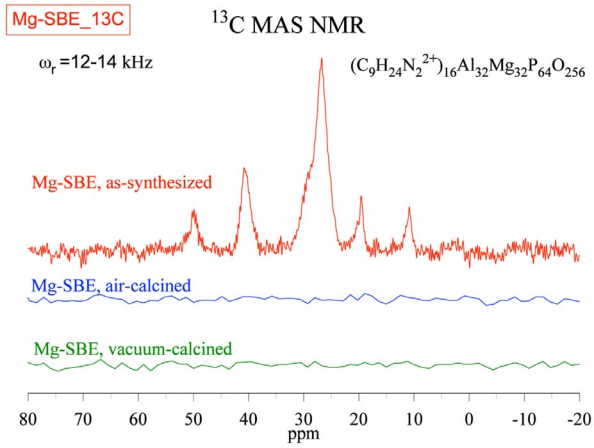
Figure S3. FT-IR spectra of SBE samples treated in vacuum at different temperatures (framework and template regions).

^{13}C MAS NMR for as-synthesized and detemplated Mg-SBE

The spectrum of ^{13}C for as-synthesized Mg-SBE exhibited peaks with chemical shifts showed in Table 2. The chemical shift of ^{13}C NMR of DAN was estimated using ChemDraw®.







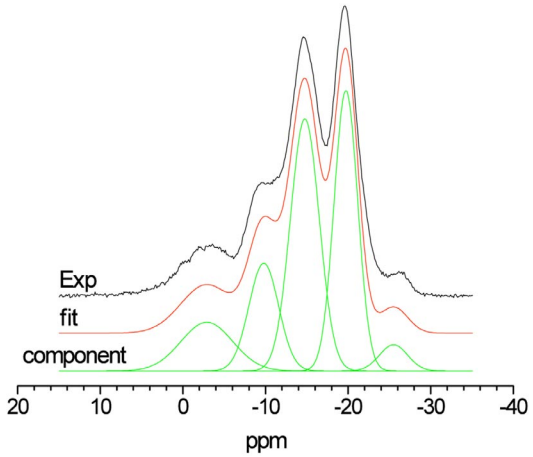
Five different carbon peaks were resolved with the same intensity except the half intensity of the center carbon of the alkyl chain. The ^{13}C NMR spectrum of Mg-SBE appears to be deviated from the expectation, especially the signal intensity around 27 ppm, which is unusually large. Assuming that the 50 ppm peak counts as one carbon, the intensity ratio reveals the relative carbon content as 1:2:7:1:1 for 50, 41, 27, 20, and 11 ppm peaks, respectively, summing up to 12 carbons. It is possible for ^{13}C NMR to show solvent peaks, and/or fragmented organic molecules. The peaks at 50, 20, and 11 ppm in ^{13}C NMR for as-synthesized Mg-SBE might be from DPA, the co-solvent, and the peaks at 41 and at around 27 ppm might be from the SDA. If the broad peak at 27 ppm is considered as one overlapped peak of the four types of carbons in SDA and the peak at 41 ppm as one from the carbon directly bonded to nitrogen, then the measured integral ratio of 2:7 between two peaks is consistent to the predicted spectrum. The measured integral ratio (1:1:1) of the peaks at 50, 20, and 11 ppm is also consistent to the predicted spectrum of DPA estimated using ChemDraw®. From the integral values of all the peaks, the amount of unreacted DPA in as-synthesized Mg-SBE sample results in half of the amount of SDA. However, we could not detect any carbon NMR peaks from the

treated samples and the ^{1}H spectra showed that there were still organic molecules present within the framework. The absence of ^{13}C peak can be explained as two possible situations: the remained organic molecules might be ammonium radicals or free radicals in the organic molecule might suppress the ^{13}C NMR signal.

^{31}P MAS NMR for as-synthesized Mg-SBE

Table SP1. ^{31}P NMR peaks of Mg-SBE

sites	Chemical shift	Intensity	Wt %
P(0Al, 4Mg)	-2.9	25286.9	12.4
P(1Al, 3Mg)	-9.8	32059.5	15.7
P(2Al, 2Mg)	-14.8	73037.6	35.8
P(3Al, Mg)	-19.7	66274.1	32.5
P(4Al, 0Mg)	-25.5	7384.3	3.6



Shifts in the ^{31}P signal are associated to structural differences due to its susceptibility to the chemical environment. A SBE-type framework consists of 4 different T sites,[1] but there are no appropriate references in the literature to help to elucidate the exact ^{31}P NMR information. Therefore, ignoring the detail site resolution, and resembling Barrie and Klinowski,[2] the observed ^{31}P NMR shifts of as-synthesized Mg-SBE sample could be assigned to P(nAl, (4-n)Mg) sites as -26, -20, -15, -10, and -3 ppm to P(4Al), P(3Al, Mg), P(2Al, 2Mg), P(Al, 3Mg), and P(4Mg), respectively. Following this analogy, signal intensities of phosphorous sites were obtained by deconvolution of the ^{31}P NMR spectrum. Assignments of the chemical shifts and the distribution percentages of each site using this approach to analyze the ^{31}P spectra are summarized in Table 4. The P(nAl, (4-n)Mg) site distribution is not in agreement with the random model which gives 6.25%, 25%, 37.5%, 25%, 6.25% for P(4Al), P(3Al, Mg), P(2Al, 2Mg), P(Al, 3Mg), and P(4Mg), respectively, when calculated using the Mg/Al ratio of 1 as predicted from the synthesis gel formulation. This may indicate the presence of ordering behavior when Mg substituted Al. The ^{31}P resolution seen for the as-synthesized Mg-SBE disappears to render only broad peak after calcinations either in air or in the vacuum. The P(0Al, 4Mg) site at -2.9 ppm appears to be resolved when calcination in air occurred .

References and Notes

(1) Baerlocher, C.; McCusker, L. B. Database of Zeolite Structures; International Zeolite Association Synthesis Commission, 2007.

(2) Barrie, P. J.; Klinowski, J. *J. Phys. Chem.* **1989**, *93*, 5972.